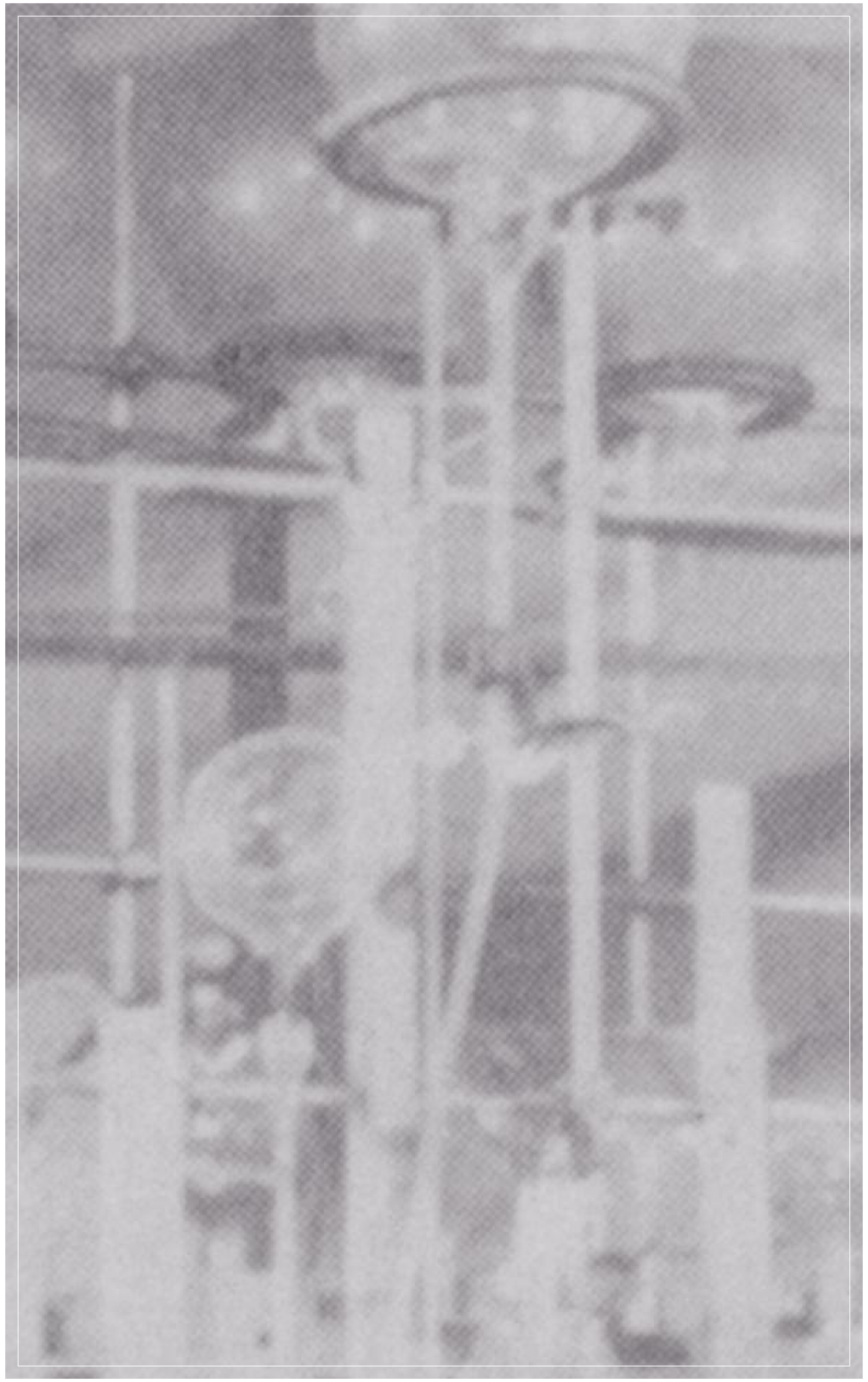


Surface sensitive spectroscopies and their impact on catalysis

> **"We observed that the electron spectra that were obtained from a certain element depended on the chemical condition of that element. We had discovered what we call 'the chemical shift'. In the beginning we didn't like this, we were physicists and wanted to study systematically the behaviour of elements. There was now a problem as we had to be careful that the substance was not oxidised or changed in some other way".**
>
> Kai Siegbahn

The period 1970-1999 witnessed astonishing advances in the ability to characterize surfaces and study reactions at solid surfaces. The chemical identity of surface species, their atomic geometries, the dynamics of their motions had become almost routinely available and mechanisms of surface reactions could be established with direct spectroscopic information on the participating surface species. Surface physics came of age and chemists were quick to take advantage in an imaginative way. Surface Science : the first Thirty Years, published in 1994, provides a useful guide as to how surface chemistry and catalysis benefited. Articles by Ehrlich, Goodman, Madey, Madix, Estrup, King, Ertl, van Hove, Somorjai and Roberts, provide an overview of the impact made by surface science during this period. Since 1994 we have also seen the very significant contribution Scanning Tunnelling Microscopy is making to our atomic level understanding of chemisorption and catalysis with contributions from Ertl, Wintterlin and Bradshaw in Berlin, Stensgaard and Besenbacher in Aarhus, Richardson and Liebsle in Liverpool, Bowker in Reading, Salmeron and Somorjai in Berkeley, Madix in Stanford and the Cardiff group (Carley, Davies and Roberts), with the latter combining STM with XPS to provide "chemical information". Structural studies also were advanced with Thomas at the Royal Institution using x-ray absorption spectroscopy, available through the Daresbury Synchrotron Source, and x-ray diffraction under reaction conditions, to provide information on the active site of a working catalyst - the ultimate in catalytic research. Having widely available synchrotron radiation make also possible the determination of surface structures through photoelectron diffraction and surface x-ray absorption fine structure (SEXAFS) studies with groups active world-wide using both single crystals and "real catalysts".

The development of surface sensitive spectroscopies heralded a new age of surface chemistry and catalysis which became synonymous with what was accepted universally as 'surface science'; the early impact it made on catalysis was reviewed by Thomson in 1978. The surface chemist took advantage of what Siegbahn (Nobel Prize in 1981) had initially perceived as a 'problem' but which by 1971 had led to the development of an ultra-high-vacuum electron spectrometer, specially designed for adsorption and catalytic studies through the cooperation of Brundle and Roberts at the University of Bradford and Yates and Latham of Vacuum Generators at East Grinstead. According to Seah and Briggs and I quote: *"It was not until the work of Brundle and Roberts in ultra-high vacuum that XPS (x-ray photoelectron spectroscopy) truly became a surface technique..."*. Other photoelectron spectrometers were also commercially available at this time and included Hewlett Packard, Perkin Elmer, Associated Electrical Industries and an earlier

Gabor A. Somorjai

(non-UHV) model (ESCA 1) from Vacuum Generators, but all these lacked the essential pre-requisite for chemisorption studies at well defined metal surfaces, namely a sufficiently low background pressure of 10^{-9} torr or less. The Vacuum Generators UHV spectrometer became widely used and was known as ESCA 3. But it was the combination of my early interest in clean surface chemistry and photoemission and Brundle's background in UV photoelectron spectroscopy of gaseous molecules (he was a student of D.W. Turner) and Vacuum Generator's commercial interest in high vacuum technology that provided the impetus for the project. There were further developments including the design of the first high-pressure spectrometer (Joyner and Roberts, 1979) which led to the next generation of spectrometers, the ESCA-LAB series. Both were funded by the Science Research Council, who had initially turned down (in 1969) the ESCA-3 project on the grounds that XPS was unlikely to be a surface sensitive technique!

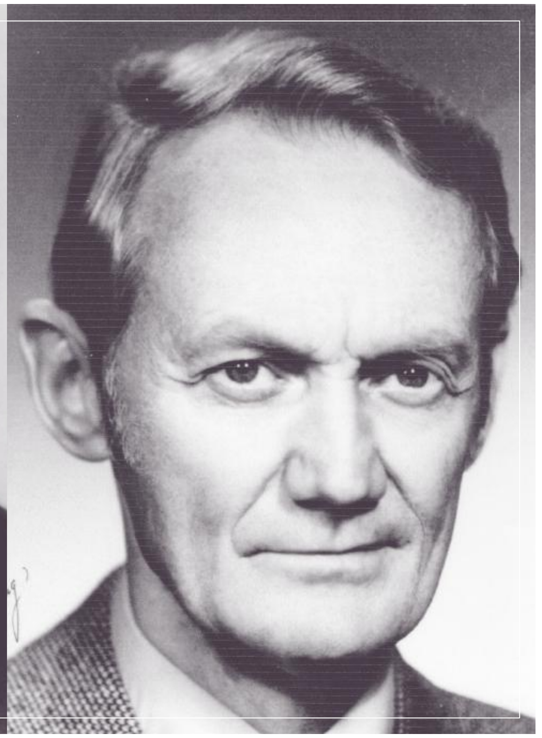
However, it was not photoelectron spectroscopy that was first to make the vital contribution to the analysis of surfaces at the "fraction of a monolayer level" but Auger electron spectroscopy. The latter, although a phenomenon first recognised in studies of x-ray induced ionisation of gaseous molecules by Pierre Auger in 1925, became available through the ingenuity of Weber and Peria who suggested how a relatively simple modification of LEED electronics allowed surface analysis to become available. There were some 30 laboratories world-wide in 1967 with LEED equipment and with relative ease could be modified to provide surface analysis. Surface chemistry and catalysis had been changed virtually overnight!

This was some 15 years after Lander had observed small peaks in the secondary-electron energy distribution function from a variety of materials which could be assigned to Auger transitions. The low sensitivity meant that the idea for it to be used for surface analysis was not pursued until first Harris in the General Electric Laboratories in Schenectady demonstrated that electronic differentiation greatly enhanced the sensitivity and second Weber and Peria's idea for modifying a LEED system to acquire Auger spectra. The electron mean escape depth, as for photoelectrons, was shown to be very short (5-20Å) and provided the chemical identification of atoms within the escape depth. This heralded the feasibility of studying the surface chemistry of well defined, atomically clean surfaces and to be able to control the chemistry through either chemical or structural modification of the surface. Palmberg described in 1968 one of the first Auger studies using a LEED system and in 1972 Brundle reviewed the applications of electron spectroscopy to surface studies. By 1978, XPS (or ESCA) was considered to be the most significant surface sensitive electron spectroscopy with ultra violet photoemission (UPS) and Auger electron spectroscopy (AES) equal second. Other surface spectroscopies beginning to make an impact were appearance potential spectroscopy, electron energy loss spectroscopy and ion-neutralisation spectroscopy. Delgass et al in 1970 reviewed the status of XPS in catalysis and included some experimental data they had acquired using the Berkeley 50cm iron-free magnetic photoelectron spectrometer. A number of points stand out: (a) it was not possible to provide spectra with binding energies assigned on the x-axis: (b) for carbon monoxide adsorption at platinum the "carbon and oxygen backgrounds were high enough to mask CO adsorption effects"; (c) the limitations of the data were due to poor vacuum conditions and (d) the count-time for acquiring a spectrum was as much as 7 hours! Nevertheless, there were promising signs for the exploitation of XPS in heterogeneous catalysis. That the authors had chosen to study NH_4Y-zeolites reflected the enormous interest that was beginning to build-up in zeolite applications in the 1960s; other spectra were of supported metals on Graphon and metal oxides and spinel catalysts (FeV_2O_4). No quantification was possible, chemical shifts were not recorded and the need for electron escape depth data emphasised. In 1971 Thomas and Barber using an AEI spectrometer reported an XP spectrum for chemisorbed oxygen present on oxidized graphite and somewhat later Thomas, then at the University College of Wales, Aberystwyth, published a comprehensive list of sensitivity data for the atomic elements.

During the early part of 1971 Brundle and Roberts at the University of Bradford established the potential of the VG ESCA-3 spectrometer, with a base pressure of 2 x 10^{-10} torr, for studying chemisorption and catalysis, with both core-level and valence-level spectra being obtained for sub-monolayer coverages of physically adsorbed water, carbon dioxide and mercury at a gold surface at 80K. These results together with the influence of surface carbon and fluorine, on the valence-level spectrum - the density of states curve - of gold, were reported at a "Discussion on the Physics and Chemistry of Surfaces" organised by J.W. Linnett and held at the Royal Society in May 1972.

One of the central features in discussions of the chemisorption of diatomic molecules at metal surfaces and addressed in the earlier work of Trapnell and later Ehrlich was whether the process was associative or dissociative. In the latter bond cleavage occurred

Gerhard Ertl



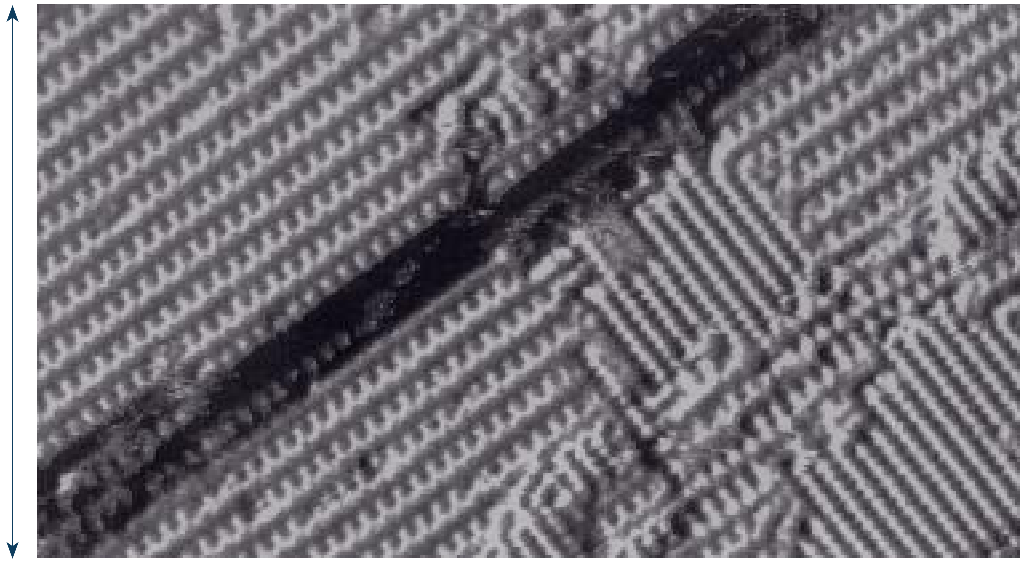
Kai Siegbahn

with obvious implications for the resulting structure of the modified metal surface. There were two different approaches in vogue during the late 1950s and early 1960s; one was to rely on infra red spectroscopy for information on the state of carbon monoxide (for example) and the second was to draw conclusions from the analysis of desorption kinetics. The infra-red studies were direct, but not necessarily unequivocal as to whether adsorption was uniquely molecular with no dissociation occurring, while, as always, kinetic studies could be ambiguous. The availability in the early 1970s for combining core-level (XPS) and valence level (UPS) photoelectron spectroscopies offered distinct advantages over these approaches at least for ascertaining whether chemisorption was uniquely associative or whether there was also a contribution from dissociative states.

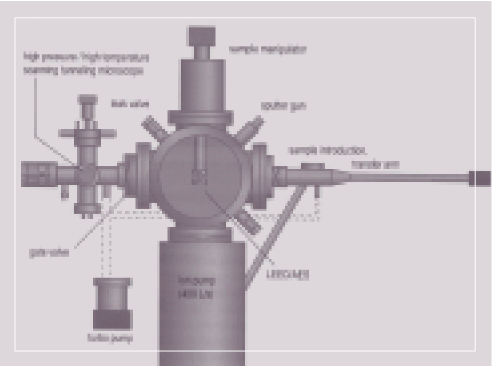
Gomer at the Faraday Discussion Meeting in 1966 highlighted the extensive studies of the adsorption of carbon monoxide at tungsten and pointed out how kinetic, field emission and electron impact desorption provided evidence for at least three types of chemisorption states. These states, described as α, β and γ, differed in their heats of adsorption, their electron desorption cross-sections and dipole moments. All states were however deemed to be molecular in agreement with the 1st order kinetics observed in Ehrlich's desorption studies. At the same meeting Holscher and Sachtler on the basis of field emission and field ion microscopic techniques suggested that a surface rearrangement of the metal atoms occurred when CO was chemisorbed and referred to it as 'corrosive chemisorption'. Furthermore the process occurred at low temperatures. The debate between Ehrlich and Holscher stimulated contributions from other laboratories - Knor in Prague, Brennan in Liverpool, Thomas in Bangor, Bassett in London - with much scepticism being suggested for the "corrosive chemisorption" concept - Brennan stating:

"I find it difficult to accept that CO molecules are able to penetrate into the subsurface region or that tungsten atoms can diffuse past adsorbed CO molecules and present new adsorption sites".

Clearly there was a strong view from many of those active in the field in 1966 that carbon monoxide was not dissociatively chemisorbed at a tungsten surface. I have given some emphasis to the carbon monoxide case as - with nitrogen - it was at that time central to both experimental and theoretical aspects of chemisorption, furthermore carbon monoxide had strong relevance to industrial catalysis whether in the context of syn-gas and Fischer-Tropsch chemistry or methanol synthesis. It was however the combination of *in situ* core and valence level spectroscopies that provided the first direct evidence for the dissociative chemisorption of carbon monoxide at metal surfaces; first with molybdenum in 1974 and in 1975 for iron. Chemical shifts in the C(1s) and O(1s) spectra together with the presence or absence of intensity from the (5σ and 1π) and 4σ orbitals in the He-induced valence spectra provided the vital clues (Kishi and Roberts 1975). It was this that stimulated renewed discussion of the Fischer-Tropsch reaction and gave more weight to the dissociative mechanism involving surface carbide rather than via the hydrocarbonyl route. At about the same time Araki and Ponec (1976) used labelled carbon (^{13}C) and also concluded that carbon-oxygen bond cleavage was the preferred route rather than via hydroxy carbene intermediates.



Atomic resolution by STM of nitrogen and oxygen adatoms present at a Cu (110) surface after the oxidation of ammonia. The nitrogen and oxygen adatoms are present in separate phases at right angles to each other (after Carley, Davies & Roberts)



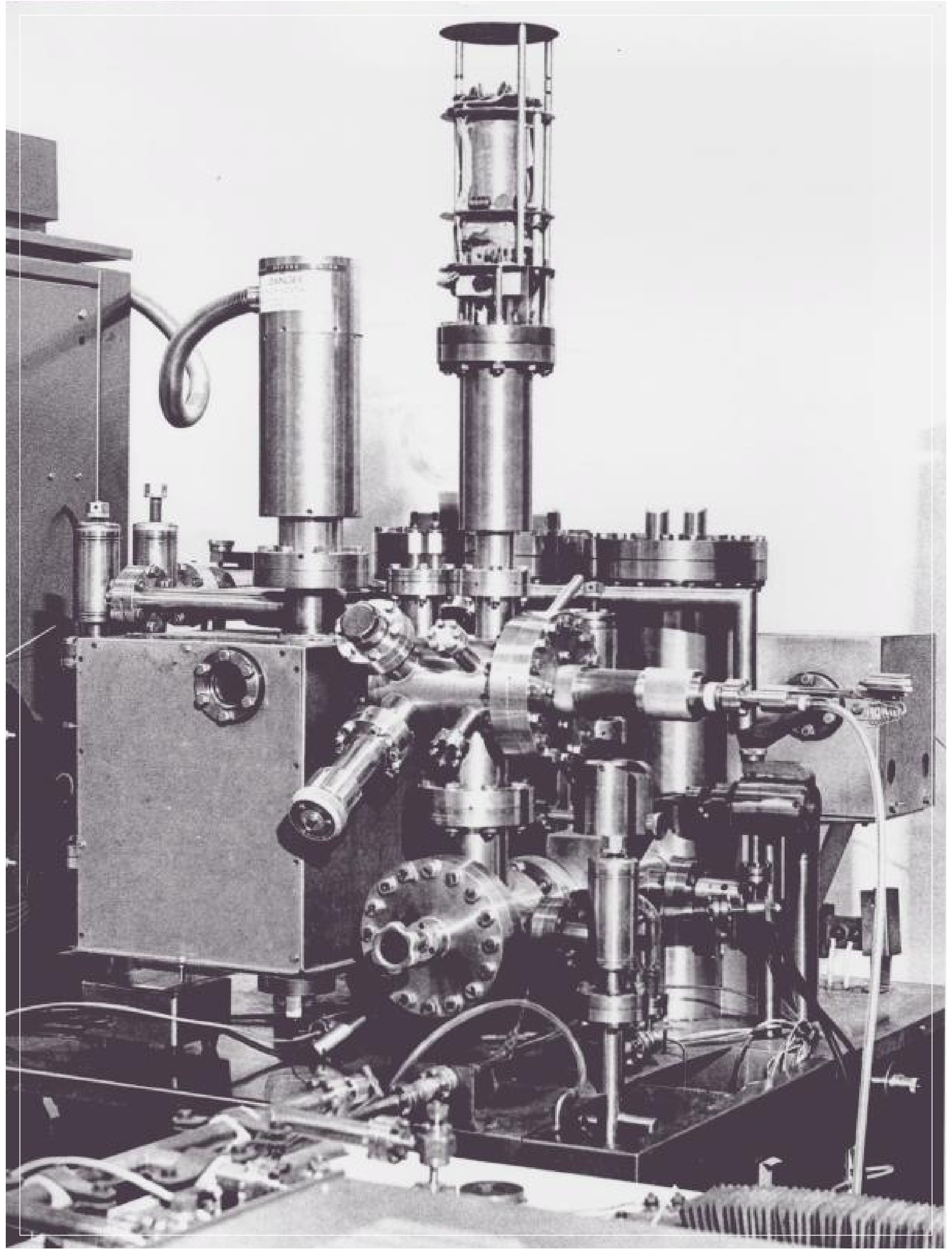
Ultra high vacuum and high pressure, high temperature, scanning tunelling microscope (after Somorjai)

What in retrospect is surprising is that a strong case was made by Webb and Eischens for CO being dissociatively chemisorbed on the grounds of CO exchange studies as early as 1955. Nevertheless more emphasis was given to the infra-red studies of Eischens and his colleagues at Texaco and Bradshaw and Pritchard in London, both groups providing evidence for molecularly chemisorbed carbon monoxide. However, infra red spectroscopy could not at that time provide evidence as to whether metal-"carbide" or metal-"oxide" bonding occurred as a consequence of the possibility that dissociative chemisorption was taking place simultaneously.

In 1964 Blyholder rationalised the diverse results available for the infra red spectra of carbon monoxide at metal surfaces by using a simple model of linear carbonyl groups with degrees of π-bonding which depended on the coordination of surface metal atoms to other metal atoms and on the availability of d-electrons for π-bonding. However, transmission spectroscopy did not allow studies of single crystal metal surfaces of defined structure and it was the development of reflection methods that provided the breakthrough in 1970 following the theoretical analysis of Greenler in 1967. Pritchard and Sims using ultra high vacuum techniques reported in 1970 the spectrum of CO adsorbed on evaporated copper films by multiple reflections between parallel mirrors; soon afterwards Chesters, Pritchard and Sims described a single reflection approach for CO adsorption on a Cu(100) single crystal. A single sharp band appeared at 2085cm^{-1} which I believe was the first infra red spectrum of CO to be observed at a metal single crystal surface. However, not all those active in heterogeneous catalysis were convinced that the surface science - single crystal approach was the way forward in catalysis with Charles Kemball expressing his views clearly and succinctly in 1970:

"I would add here a plea to those who are fascinated by ultra high vacua and work with single crystals to remember that there is a danger they may become imprisoned in their own ivory towers".

By 1988 when Sheppard reviewed vibrational spectroscopic studies of the structure of species derived from hydrocarbon chemisorption on metal single crystal surfaces the literature had become voluminous. Furthermore results from single crystals by the RAIRS technique were particularly valuable in that they were useful for the interpretation of vibrational spectra obtained from hydrocarbons adsorbed on finely divided metal particles usually supported on metal oxides. The infra red spectra indicated that with increasing temperature



Ultra high vacuum and high pressure, high temperature, scanning tunelling micioscope

more and more hydrogen is driven off but prior to this many hydrocarbons have very similar spectra consisting of absorptions at between 750 and 840 and near 3030cm^{-1}. These frequencies led to the suggestions that the residual species is CH with the two absorptions representing νCH and δCH modes respectively. In between the high and low temperature regimes of adsorption there were reported a variety of intermediate chemisorbed species of which the ethylidyne CH_3C attracted considerable attention when it was first suggested to arise from ethylene chemisorption. Although reflection absorption infrared spectroscopy was initially performed using dispersive spectrometers Fourier transform techniques were introduced in the early 1980s leading to the acronym FT-RAIRS. The advantages of FT over dispersive techniques were two-fold - improved signal to noise ratios and all spectral features are recorded simultaneously. FT-RAIRS also had distinct advantages over high resolution electron energy loss spectroscopy (HREELS) in that it had much better resolution, 2cm^{-1} compared with 60-70cm^{-1}, although very recently (in 1997) the new Ibach spectrometer was capable of a resolution very competitive with FT-RAIRS. However, a significant advantage of FT-RAIRS was the ability to record spectra at "high pressures" making it particularly valuable for the study of heterogeneously catalysed reactions. By the early 1990s FT-RAIRS has been so well developed, that although not entirely routine, it had evolved to the point that it was accessible to most laboratories with an interest in surface science and catalysis - but care has to be taken when high pressures are used as interference from the gas phase can become a problem.

In 1994 King in reviewing developments in chemisorption over the last 30 years referred to *"the wilderness of heterogeneous catalysis, the corner stone of the chemical industry and one of the remaining bastions of empiricism, is beginning, reluctantly one senses, to give way to the encroachments of high technology"*. My personal view is that a step change in the approach to heterogeneous catalysis took place somewhat earlier, nearly thirty years ago. First with the emergence of surface sensitive spectroscopies which enabled real-time studies of surface processes at solid surfaces of well defined composition and second with the development of experimental methods that bridged the pressure-gap. Somorjai pioneered this approach and made possible high quality fundamental studies under conditions which were close to those operating in real catalysis with Joyner and Somorjai exposing the role of surface steps in molecule activation. Somorjai was the recipient of the Kendall Award in 1981 *"...for his imaginative and stimulating work on the structure of catalytic surfaces and adsorbed layers as well as the study of reactions proceeding on the surface"*. In order to unravel the molecular ingredients of heterogeneous catalysis he developed experimental methods which combined catalytic reaction rate studies carried out at several atmosphere pressure with surface analysis of the catalyst that usually required ultra-high vacuum conditions. It was established that platinum single crystals served as excellent model catalysts; LEED provided structural information, flat terraces could be prepared with steps one atom high, kink sites could be introduced and their catalytic activity recognised in (for example) hydrocarbon conversion reactions. The concept of structural sensitivity could be examined at the atomic level for the first time!

In an article in Advances in Catalysis in 1977 Somorjai described the "low pressure - high pressure" apparatus which enabled surface reaction rates in the pressure range 10^{-7} torr to 10^{5} torr to be studied at single crystal surfaces (1 cm^2 area). There was also *in situ* facilities for structural information to be obtained from LEED and surface chemical analysis by Auger electron spectroscopy. In the same article Somorjai drew attention to the significance of molecular beam surface scattering experiments where a well collimated beam of the reactant gas or gas mixture is scattered from a crystal surface and the products that are desorbed after a single scattering at a given solid angle are detected by mass spectrometry. Detailed kinetic information for both the adsorption step and the surface reaction step leading to gaseous products could be obtained, the overall aim being to ascertain the nature of active sites in heterogeneous catalysis.

In addition to the considerable interest in the surface chemistry of dinitrogen in the 1960s, as the archetype of dissociative chemisorption, there was also the impetus of the need to understand at the molecular level the mechanism of the Haber-Bosch process. Clearly the emergence of surface sensitive spectroscopies provided an obvious way forward whereas during the previous 50 years suggested mechanisms had been based on kinetic studies coupled with thermodynamic arguments.

Emmett in 1974 states when discussing progress in the study of ammonia synthesis: "The experimental work of the past 50 years leads to the conclusion that the rate - determining step at iron catalyst surfaces is the chemisorption of nitrogen. The question as to whether the nitrogen species involved on the surface is molecular or atomic is still not conclusively resolved, though in the writer's opinion, the direct participation of nitrogen in the atomic form seems more likely than in the molecular form." In 1991 Ertl concluded that "as a consequence of the availability of surface science techniques developed since 1970 (or thereabouts) a microscopic picture of the catalytic reaction with a quantitative predictive character for the high pressure conditions of industrial practice has been more or less reached."

How then was this conclusion arrived at?

X-ray photoelectron spectroscopy was used first in 1977 to explore whether different adsorption states of nitrogen were present at polycrystalline iron surfaces. Two N(1s) peaks were reported by Kishi and Roberts with binding energies of 400.2eV and 405.3eV at 85K and assigned to a molecular state(s) whereas at 295K there is a single N(1s) peak attributed to chemisorbed nitrogen adatoms. In a later paper Johnson and Roberts reported that the molecular state *"converted slowly to the atomic state"* at 80K and suggested that it was this transformation that was responsible for the very low sticking probability (10^{-7}) of the chemisorption step at 295K. The activation energy for the transformation was low but the concentration of the molecular precursor state at 295K, due to its low heat of adsorption, would be very small. It was an example of precursor state control of reaction rate, confirming the much earlier sticking probability-coverage-temperature behaviour of nitrogen chemisorption at tungsten or molybdenum surfaces.

In 1982 Ertl, Lee and Weiss reported three distinct nitrogen states at Fe(111) surfaces, two molecular states one (γ) which desorbed at 100K and the other (α) at 150K and an atomic state. The latter resulted from the dissociation of the α state on warming. The sticking coefficient of nitrogen varied for various planes of iron but the presence of potassium both increased the rate of dissociative chemisorption and resulted in the inherent differences between the atomically clean crystal planes being eliminated. An electrostatic model was proposed. Ertl in 1991 reviewed the position and proposed a mechanism for the synthesis of ammonia with support from both spectroscopic and theoretical modelling of the kinetics observed at iron single crystal surfaces. In addition to the Ertl approach two other kinetic models, one by Bowker, Parker and Waugh and the other by Stoltze and Nørskov are discussed with claims that the single crystal and real catalyst data are reproduced by the Stoltze-Nørskov model. Central to all the models is the assumption that dissociative chemisorption of nitrogen is rate-determining.

Somorjai was the first to show in 1982 that at 20 atm pressure and 773K using a 3:1 H_2:N_2 mixture the synthesis activity varied with surface structure in the order (111)>(100)>(110) and that seven-coordinated metal atom sites (C7) available only on active surfaces control the reaction rate under most experimental conditions. Somorjai also took the view that if progress was to be made then it was important to mimic in surface science studies the catalyst used under real synthesis conditions. One of the most significant discoveries to emerge from this approach was that surface restructuring occurred relatively early in the presence of alumina, furthermore water vapour could also play a role. The process by which iron restructures involves both oxidation and reduction, with the active planes for synthesis Fe(111) and Fe(211) being generated. The role of the support phase (Al_2O_3) is to stabilise these active planes and prevent their re-conversion to less active orientations. Somorjai and his colleagues were in 1987 the first to provide direct experimental proof for what had been put forward as a possibility by Ozaki in 1981. More recently, in 1994, Somorjai and Materer reviewed the significant role of surface structure in ammonia synthesis and drew attention to the need to carry out high pressure/high temperature STM studies using both Fe(111) and Fe(211) surfaces to explore the dynamic changes that occur during synthesis.

In spite of the considerable effort mode to provide a satisfactory model for ammonia synthesis Spencer argued in 1992 that the following three steps may be rate determining under various synthesis conditions

$$N_2(g) \rightarrow N_2(a) \rightarrow 2N(a) \qquad (1)$$

$$N(a) + H(a) \rightarrow NH(a) \qquad (2)$$

$$NH_3(a) \rightarrow NH_3(g) \qquad (3)$$

Only at low pressures can a single rate-determining step, reaction (1) be identified and for higher pressures this assumption is invalid, while under industrial conditions reactions (2) and (3) are considered to be more significant in controlling synthesis rate. Furthermore Spencer expresses some concern regarding the use of modelling to fit a given set of kinetic data and thereby provide evidence for an "unambiguous mechanism". Somorjai's approach appears the most likely to provide a satisfactory answer to the ammonia synthesis problem which has been a testing ground for concepts in heterogeneous catalysis throughout the last century - his central tennet being the role of the "flexible surface structure" in the creation of the "active site".

The most recent contribution to the mechanism of ammonia synthesis that I am aware of has been made by Waugh at Manchester. The approach adopted was similar to that which had been used in the early 1970s, the microkinetic analysis of heterogeneous reactions to predict the performance of an industrial naptha cracker. In his recent paper Waugh discusses the extrapolations that had to be made from Ertl's surface science data to the industrial conditions: 600K of temperature and 10^{14} in pressure and examines the validity of the extrapolation and various parameters implicit in the ammonia synthesis mechanism. The paper is persuasive and to account for the yield over an industrial catalyst the analysis "predicted the need for the activated dissociation of the molecular nitrogen precursor state"; this was observed by Fastrup in 1994 in agreement with Waugh's prediction in 1985. For those closely involved in the ammonia synthesis problem there is a detailed analysis by Waugh of Ertl's data, industrial data and earlier efforts to fit these experimental data with theoretical models including those of Stoltze and Norskov. In the same paper Waugh examined the method of microkinetic analysis to the forward and reverse water gas shift reaction. One aspect of the analysis in which I had a particular interest was that "the surface of the copper which is catalysing the reaction is covered by oxygen atoms to an extent which is dependent on the detailed kinetics of the adsorption of hydrogen. The adsorption of CO_2 on this area of surface oxidized copper will produce a surface carbonate". Oxygen activation of various adsorbates had been first recognised in the mid 1970s by XPS including CO_2 by low coverages of oxygen, the surface oxygen in the water gas shift reaction being a consequence of water dissociation followed by dehydroxylation.

Over the last 30 years surface spectroscopies have made a profound contribution to the catalytic chemistry of hydrocarbons. Early studies by Eley, Rideal, Bond, Kemball, Boudart, Sachtler, Rooney, Sinfelt and Gault were in the main based on kinetic analysis which provided somewhat indirect evidence for reaction mechanisms. In the 1960s surface spectroscopy provided a more direct approach with the possibility of very basic chemical transformations being able to be characterised in model systems. Much attention has been given to the chemisorption of unsaturated hydrocarbons on single crystal metal surfaces and also the activation of alkanes by metals. These are areas where Somorjai and van Hove have been at the forefront starting in 1969 with LEED information for hydrocarbon adsorption on Pt(111) and Pt(100). The chemisorption of ethylene at Pt(111) has become a classic example, adsorbing in the molecular state at low temperatures, first as a flat π-bonded species but then rehybridize above 52K into another flat di-σ configuration. On heating the ethylene decomposes through a series of competing reactions with RAIRS evidence for the formation of ethylidyne at room temperature. The reaction mechanism is still in some doubt but it appears that the likely intermediate is ethylidyne, with LEED providing (in addition to RAIRS) important structural information. Ethylidyne has so far been identified on Pt(111), Pt(100), Rh(111), Rh(100), Pd(111), Ru(0001) and Ir(111) single crystals as well as on supported platinum, palladium and nickel catalysts. In addition the formation of higher alkylidynes - n-propylidyne to n-pentylidyne - has also been reported.

Catalytic surface science studies relied very much on what is referred to as the 'sample-transfer procedure' and therefore did not address the problem of the "pressure-gap". More recently second harmonic generation (SHG) and sum frequency generation (SFG) have provided a break through in overcoming the pressure-gap problem with Somorjai in 1995 showing its advantage in the Pt(111)-ethylene system where in addition to ethylidyne there is also shown to be present weakly π-bonded ethylene which is hydrogenated to ethane. The advent of STM as an important tool in surface catalysis has also been illustrated by Somorjai in surface oxidation reactions. Zaera has reviewed the present status of hydrocarbon surface chemistry - emphasising the contributions of Gabor Somorjai a recipient of the Wolf Prize in 1998 jointly with Gerhard Ertl.

That alkane activation at metal surfaces was difficult was well recognised but it was Stewart and Ehrlich in 1975 who revealed that it was the vibrational modes are the most likely source of energy for the dissociation of methane on rhodium while more recent work by Madix and Weinberg reported that only the normal component of the translational energy of the alkane is important for the C-H bond breaking step in supersonic beam experiments. Surface structure is also an important factor in activation as substantiated by Weinberg in 1993.

Bond-making and bond-breaking, particularly at low temperatures (80K-300K), was an area to which we gave much attention during the 1970s with studies of the reactive chemisorption of nitric oxide leading to the formation of N_2O at both sp and transition metals providing insights into the mechanisms of metal catalysed reactions which were conceptually different from classical Eley-Rideal and Langmuir-Hinshelhood models. Chemisorbed metastable oxygen states present at low temperatures were shown to exhibit high reactivities in oxydehydrogenation reactions and provided an impetus for more detailed studies of the activation of molecules by specific oxygen 'transient' states. How the chemisorbed 'oxide' layer formed and what was the nature of the reactive sites were not questions being pursued by the surface science community at large, more attention being given to structural aspects of the thermodynamically stable 'oxide' overlayer using EXAFS and SEXAFS.

Mention has already been made to the possible role of oxygen transients in providing low energy pathways in elementary steps involved in surface catalysis and not available via surface oxygen when in the final chemisorbed 'oxide' state. This was first recognised in co-adsorption experiments carried out in 1986 in Cardiff where ammonia-rich dioxygen-ammonia mixtures were used in the study of ammonia oxidation at magnesium surfaces. The role of oxygen transients in the formation of amide and imide species by an oxy-dehydrogenation reaction - with the analogy made with the highly efficient, low energy abstraction gas phase reaction - was a new concept in the interpretation of the mechanism of surface reactions. It is neither an Eley-Rideal nor a Langmuir-Hinshelwood mechanism, although Pritchard at the Faraday Symposium held in Bath in 1986 suggested "that in the limit the transient oxygen atom reaction with ammonia undergoing rapid surface diffusion could approximate to the Eley-Rideal model". The Cardiff group over the next decade established this to be of wide ranging significance and was taken up theoretically by van Santen, emphasised by Haber in a review in 1994 and extended by Iwasawa in 1997. The driving force for this work was to understand catalytic oxidation reactions using surface sensitive spectroscopies, where the two reactants - one of which was oxygen - were exposed to the "catalyst surface" simultaneously. The possible role of oxygen transients followed and the life-time of the reactive oxygen transient $O^{\delta-}$ was defined as the time it existed under reaction conditions before it became converted with increasing coverage into the relatively unreactive 'oxide species' $O^{2-}_{(a)}$. Whether the reactive transient was atomic $O^{\delta-}$, or molecular, $O^{\delta-}_2$, depended on the dynamics of the chemisorption process and therefore on the metal. Furthermore reaction pathways could be controlled by varying the oxygen composition of the gas mixture (O_2:NH_3; O_2:H_2O); O_2:hydrocarbons; O_2:CH_3OH) as shown by publications from both Cardiff and C.N.R. Rao's group in Bangalore.

It was, however, Madix at Stanford, using STM who established that in the oxidation of ammonia at copper surfaces the model established by the Cardiff group was sustainable when viewed at the atomic level. More recently STM facilities became available at Cardiff and the models for surface reactions based on surface sensitive spectroscopies have been tested further with both dioxygen and atomic oxygen species implicated as the reactive species. Bowker at Reading also appreciated the significance of coadsorption studies and pursued, using STM, the atomic approach to unravelling the mechanism of surface catalysed oxidation reactions. That metastable or non-equilibrium oxygen states $O^{\delta-}$ or $O^{\delta-}_2$ present at metal surfaces, prior to the formation of the final chemisorbed state, exist there is no doubt, with Ertl's group in Berlin being at the forefront. What is not clear is the reason for their high reactivity. In the case of $O^{\delta-}_2$, precursor states involving charge transfer complexes of the type ($O^{\delta-}_2$--- NH_3) provide low energy reaction pathways to oxidation products. On the other hand atomic transients $O^{\delta-}$ were suggested to be O^--like and therefore isoelectronic with fluorine and expected to show high chemical reactivity. In the Nature paper of 1986 the atomic oxygen transients present at Mg(0001) surfaces were suggested to undergo rapid surface diffusion subsequent to bond cleavage. Support for this has come from the STM data of Ertl and Wintterlin who studied the Al(111)-oxygen system and Ceyer's observation of ballistic motion of fluorine atoms when F_2 chemisorbs at a silicon surface. In this context it is also pertinent to mention the observations of Ceyer where hydrogen appearing at the surface of Ni(111) from *within the solid* exhibits very different hydrogenation activity to chemisorbed hydrogen present *at the surface*. This Ceyer attributes partly to their large difference in energy, the analogy with "hot" O-adatoms generated by dissociative chemisorption of oxygen and first recognised at Mg(0001) surfaces in their oxydehyrogenation activity, is compelling with Ertl also reporting the escape of O^- ions when oxygen chemisorbs at cesium surfaces. Waugh has also drawn attention to the uniquely selective oxidation behaviour of lattice oxygen when it appears at the surface of vanadyl pyrophosphate.

Although the recognition of spatio-temporal patterns forming far from equilibrium is a widespread phenomenon in nature its relevance to heterogeneous reactions is relatively new. Ertl has, however, studied the oscillating behaviour of CO oxidation at Pt(110) surfaces and the conditions necessary for their behaviour delineated; these include the pressure of CO, the coverages of oxygen and carbon monoxide and temperature. In this study the advantage of the photoemission electron microscope in being able to observe spatio-temporal patterns is particularly significant. Understanding, control and exploitation of self-organising processes on solid surfaces may well become one of the key technologies of the next century.

A theme which Somorjai has championed is the idea of the flexible surface - restructuring in the ammonia synthesis reaction being just one example. The Cardiff group has, for example, shown using STM how a molecule such as pyridine can effect an increase in the spacing between copper-oxygen rows when chemisorbed, the process being reversible and relaxing to the original inter-row spacing when the pyridine desorbs. The dynamic nature of the solid surface and the associated chemisorbed species is undoubtedly one of the most significant new concepts with precise experimental verification at the atomic level that have emerged over the last decade and will have a profound influence on thinking in mechanistic aspects of surface catalysed reactions. Atomic resolution using STM has provided, at least in principle, the ultimate test for exploring reaction mechanisms at solid surfaces with Somorjai extending the technique to include reactions at high pressure and high temperature. Very recently at the ACS Meeting in Anaheim, California, in March 1999, Somorjai reminded us of Kemball's warning nearly 30 years ago (see above) and I quote:

"If surface science is to maintain its credibility in the field of catalysis it is time that we leave the comfortable world of single crystals and turn to the more realistic supported particles".

I believe Charles Kemball who died in 1998 would have been delighted to have read this!

However, progress is already being made in this direction both by Somorjai and also in the laboratories of Goodman, Gai, Schlogl and Freund through modelling catalysts by growing thin oxide films on single crystal metal surfaces and also supporting metal clusters on oxides.

Although "surface reconstruction" was not readily accepted by the academic community - the debate regarding "corrosive chemisorption" in the 1960s being a manifestation of this reluctance - it is now a central part of current catalytic thinking. A good example is the reconstruction of platinum clusters in zeolite cages when exposed to different pressures of carbon monoxide. Using FTIR, Stakheev, Shpiro, Jaeger and Schulz-Ekloff (Catalysis Letters, 34, 293, 1995) showed that the platinum particles are converted into neutral platinum carbonyls stabilised by the basic oxygen atoms of the zeolite framework. The process is reversed on decreasing the CO pressure.

That single component metal catalysts were not necessarily the best was shown through the work at Exxon of Sinfelt and his colleagues where substantial improvements in the performance of reforming catalysts could be achieved through the development of bimetallic platinum-iridium catalysts. Almost simultaneously the Chevron Oil Company (in the early 1960s) had developed platinum-rhenium catalysts. Both catalysts were more efficient than "pure" platinum in the hydrogenolysis of carbon-carbon bonds thus diminishing surface poisoning by carbonaceous species. These were significant breakthroughs in both catalytic technology and fundamental concepts of catalyst behaviour.

It was indeed studies of alloy catalysts that led to the demise of the electronic theory of catalysis with a Dutch group (Surface Science 18, 62 1969) establishing that the composition of alloy surfaces could be substantially different from the corresponding bulk composition. The "collective" approach to catalysis was replaced by the "atomistic" approach leading to the emergence of such new concepts as "ensemble effect", "ligand effect" and "structural sensitivity". A good account of these developments is to be found in the book by Ponec and Bond.

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